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Mechanistic Investigation into the Decarboxylation of the Sodium, Potassium, and Calcium Salts of Aromatic Carboxylic Acids and Their Role in Cross-Linking Reactions

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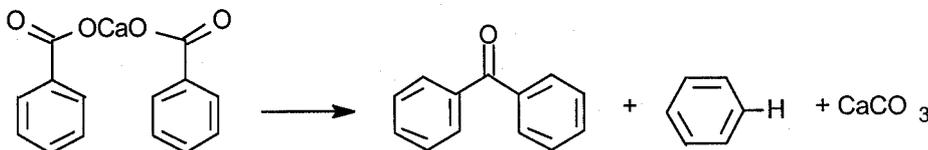
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Introduction

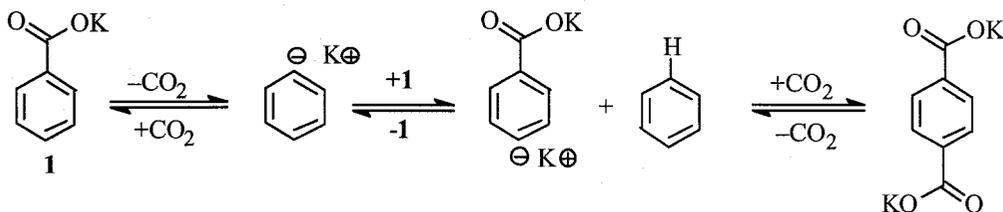
It is well recognized that cross-linking reactions occur during the pyrolysis and liquefaction of coal, and that these reactions lower the yield of liquid products. Cross-linking reactions are rank dependent with low-rank coals, such as lignites and subbituminous coals, cross-linking at lower temperatures than bituminous coals.¹ Oxygen functional groups, such as carboxylic acids and phenols, have been implicated in cross-linking reactions, since low-rank coals contain high concentrations of oxygen, 15-30 wt% on dmmf basis, and weathered coals show reduced tar yields in pyrolysis.² Cross-linking reactions have been correlated with loss of carboxyl groups and evolution of CO₂ and water.^{1,3} Pretreatments such as demineralization or methylation reduce cross-linking, while ion-exchange of Na⁺, K⁺, Ca⁺², or Ba⁺² into demineralized low-rank coal increase cross-linking.^{4,5,6} The extent of tar yield reduction in the pyrolysis of low-rank coal has also been shown to be directly related to the extent of cation exchange of the coals' carboxyl groups, and alkali and alkaline earth metal cations have been shown to change the aromatic/aliphatic composition of the pyrolysis tar.^{7,8} The reduction in tar and liquefaction yields by divalent cations has been attributed to cross-links formed between the carboxylic acids and the metal cations in the coal matrix.^{1,8}

Despite the numerous studies on the impact of carboxylic acids and their salts on the pyrolysis, combustion, and liquefaction of low-rank coals, the mechanistic origins of cross-linking are still poorly understood. To provide fundamental information on the decomposition of aromatic carboxylic acids and their salts, we have investigated the pyrolysis mechanisms of simple and polymeric model compounds containing aromatic carboxylic acids.^{9,10} From these investigations, it was determined that decarboxylation of aromatic carboxylic acids, such as benzoic acid and dibenzoyldicarboxylic acid, occurred primarily by an acid promoted ionic pathway that does not lead to a significant amount of cross-linking (i.e., higher molecular weight products). However, in nondonor solvents (such as naphthalene), a small amount (<3 mol%) of cross-linked products (i.e., phenylnaphthalene) was formed.^{9c} These cross-linked products arose from the condensation of the carboxylic acids to form aromatic anhydrides, which can undergo a free radical induced decomposition reaction to form aryl radicals that abstract hydrogen or add to aromatic rings to form arylated products. Water and hydrogen donor solvents were found to decrease the formation of cross-linked products by hydrolysis of the anhydride and hydrogen transfer to the aryl radicals, respectively. Although anhydride formation was minor in the pyrolysis of these simple model compounds, anhydride formation was dominant in the pyrolysis of a polymeric model compound, poly-(1,3-xylylene-*co*-5-carboxy-1,3-xylylene), that contained 2.3 carboxylic acids per 100 carbons similar to the concentration of acids found in Beulah-Zap lignite coal.^{9b}

The pyrolysis of salts of carboxylic acids has also been investigated.^{9a,10} Sealed tube pyrolysis of the dipotassium salt of 1,2-(3,3'-dicarboxyphenyl)ethane at 400 °C for 30 min neat, in tetralin, or in naphthalene produced no products, and the starting material was recovered unchanged. Calcium benzoate was also found to be relatively stable at 400 °C (0.05% conversion to benzene after 1 hr). Small amounts of water did not affect these sealed tube pyrolysis results. However, if benzoic acid was mixed with calcium benzoate, an increase in the rate of decarboxylation was observed that was proportional to the amount of added salt. This observation was consistent with the ionic decarboxylation pathway. To gain more insight into the temperature at which the alkaline and alkaline earth metal salts of aromatic carboxylic acids decompose, the pyrolysis of the sodium, potassium, and calcium salts of benzoic acid was investigated by thermogravimetric analysis with mass spectrometric analysis of the evolved gases (TG-MS). At a heating rate of 5 °C min⁻¹ under argon, all the benzoate salts show a major weight loss at 509 ± 2 °C, although the shape of the derivative curves (DTG) was different for each sample. It was proposed that calcium benzoate decomposed by a free radical pathway to form benzophenone (by coupling of the benzoyl and phenyl



radicals), benzene (from hydrogen abstraction by the phenyl radical), and CaCO_3 .^{10,11} At higher temperatures ($>600\text{ }^\circ\text{C}$), the CaCO_3 decomposed to CaO and CO_2 . The potassium and sodium benzoates were proposed to decompose by an uncatalyzed Henkel Reaction (i.e., anionic decarboxylation/disproportionation to benzenedicarboxylic acid and benzene) and a free radical reaction pathway that leads to cross-linked products, such as phenylbenzoate, and char.¹² Although the reaction pathways for product formation are not completely resolved, decarboxylation of the salts occurs at higher temperatures than the acid and cross-linked products are observed with all the substrates.



In this investigation, the TG-MS of random copolymers of styrene and vinylbenzoic acid was investigated as a function of acid content to determine the impact of the polymer matrix on the decarboxylation of the acids and the salts. These polymers were chosen since these are easy to prepare by free radical polymerization, and the decomposition pathways of polystyrene have been investigated so the impact of the salt on the reaction pathways could be determined.¹³

Experimental

Carboxy-terminated polystyrene was obtained from SP^2 ($M_w = 9940$). Copolymers of styrene and vinylbenzoic acid were prepared by free radical polymerization as previously described.¹⁴ For poly(styrene-*co*-vinylbenzoic acid) with 2.3, 4.7, and 19.3 mol% vinylbenzoic acid, the molecular weights were 13,500; 17,600; and 11,970, respectively. The salts of the acids were prepared by adding stoichiometric amounts of base (NaOH , KOH or CaH_2) to a THF solution of the copolymer followed by precipitation into hexanes and drying. FTIR analysis confirmed the presence of the salts by disappearance of the free and hydrogen bonded $\text{C}=\text{O}$ stretch at 1734 and 1688 cm^{-1} , respectively.

TG-MS measurements were made on a TA Instruments Model 2050 thermogravimetric analyzer connected to a Balzers ThermoStar mass spectrometer (0-300 amu) through a heated ($200\text{ }^\circ\text{C}$) transfer line as previously described.¹⁰ Samples were weighed in platinum pans and the samples were purged with argon (100 mL min^{-1}) until the oxygen levels stabilized (ca. 1-3 h, typically $<50\text{ ppm O}_2$). The samples were heated at $5\text{ }^\circ\text{C min}^{-1}$ from room temperature to $800\text{ }^\circ\text{C}$. All measurements were repeated, and the transition temperatures and residue yields were reproducible.

Results and Discussion

The styrene-*co*-vinylbenzoic acid polymers were pyrolyzed in a TG-MS at a heating rate of $5\text{ }^\circ\text{C min}^{-1}$ to a final temperature of $800\text{ }^\circ\text{C}$ under argon. As the acid content of the copolymers increased from 0, 2.3, 4.7, 19.3, to 100 mol%, the residue at $600\text{ }^\circ\text{C}$ increased from 0.2, 0.4, 0.5, 4.6, to 29.3 wt%, respectively. Except for poly(vinylbenzoic acid) (PVBA), these polymers had a major weight loss at $410 \pm 6\text{ }^\circ\text{C}$ which corresponded to depolymerization of the polystyrene backbone (to form predominately styrene, but α -methylstyrene and toluene were also observed).¹³ The TGA trace for PVBA had a small weight loss (6.4 wt%) centered at $338\text{ }^\circ\text{C}$, corresponding to the loss of water from the formation of anhydrides, and a major weight loss at $447\text{ }^\circ\text{C}$ (61.3 wt%) from depolymerization of the polystyrene backbone. The methyl esters of these copolymers cleanly depolymerized and no residue ($<0.1\text{ wt}\%$) was found at $600\text{ }^\circ\text{C}$. This highlights that the acids are responsible for the formation of the nonvolatile residue (which are most likely cross-linked products from arylation reactions) as previously reported.^{9b}

The sodium and the potassium salts of the copolymers were also investigated by TG-MS. In all cases, the salts produced more residues than the free acid and the weight of the residue was greater than that expected from the weight of cation alone. For example, the sodium salt of the 4.7, 19.3, and 100 mol% vinylbenzoic acid copolymers produced 6.4, 33.0, and 58.9 wt% residue at $600\text{ }^\circ\text{C}$, respectively. The TGA trace of the sodium salt of poly(styrene-*co*-19.3% vinylbenzoic acid) and its acid form is shown in Figure 1. The major weight loss for both polymers occurs at $417\text{ }^\circ\text{C}$, corresponding to depolymerization of the polystyrene backbone, but a new shoulder is observed at $513\text{ }^\circ\text{C}$ for the salt. This temperature is similar to that observed for the decarboxylation of sodium benzoate ($511\text{ }^\circ\text{C}$).¹⁰ The TGA trace of the sodium salt of PVBA has one major weight loss at $511\text{ }^\circ\text{C}$. This indicates that although the polystyrene backbone depolymerizes before decarboxylation of the salt, the nonvolatile salt can not diffuse out of the sample until decarboxylation releases styrene. Thus, the organic fragments attached to the carboxylate salt are exposed to temperatures more than $60\text{ }^\circ\text{C}$ higher than found for the free acid. This restricted mobility provides the opportunity for additional cross-linking reactions, which would lower the yield of volatile products. As the concentration of the salt decreases, two transitions are observed in the copolymers: one at ca. $410\text{ }^\circ\text{C}$ for depolymerization

of the styrene backbone and one at ca. 510 °C for the decarboxylation of the vinylbenzoic acid salt (as shown in Figure 2). The TGA curve for the calcium salt of poly(styrene-*co*-4.7% vinylbenzoic acid) was very similar to that of the sodium salt with

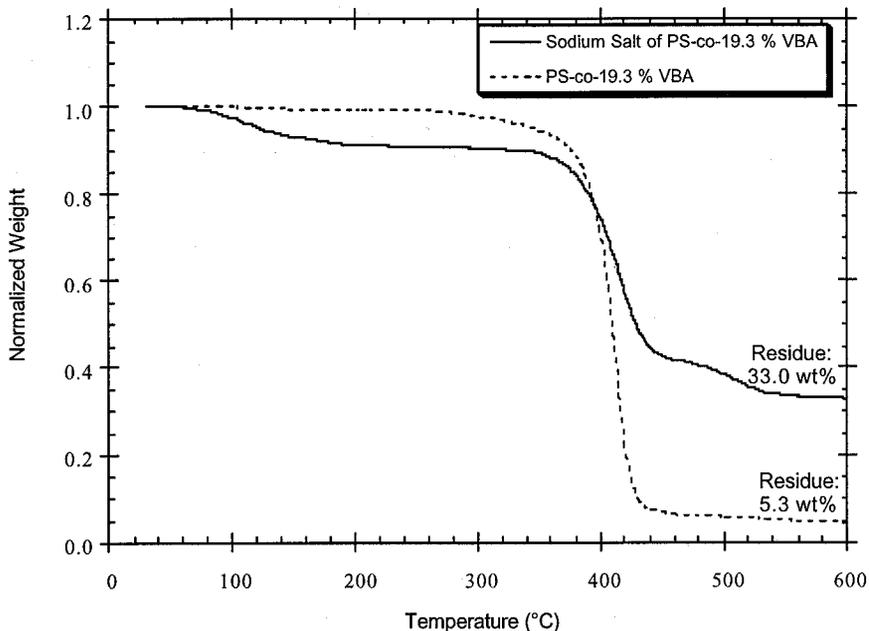


Figure 1. TGA of poly(styrene-*co*-19.3% vinylbenzoic acid) and its sodium salt.

weight losses at 407 °C (88.0 wt%) and 480 °C (2.5 wt%). Surprisingly, slightly fewer residues were found for the calcium salt (5.2 wt%) than the sodium salt (6.4 wt%) at 600 °C. We are currently preparing and studying the decomposition of additional calcium exchanged copolymers to determine the impact on cross-linking and char formation.

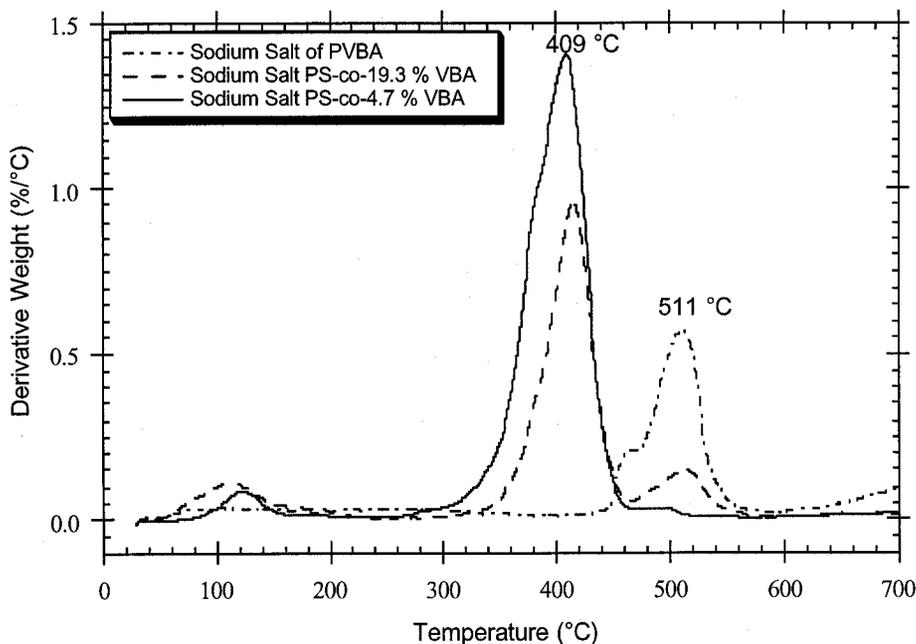


Figure 2. DTG of the sodium salt of polyvinylbenzoic acid (PVBA), poly(styrene-*co*-19.3% vinylbenzoic acid), and poly(styrene-*co*-4.7% vinylbenzoic acid).

Conclusion

The reaction pathways for the decomposition of aromatic carboxylic acids and their sodium and potassium salts were investigated by TG-MS. As the content of carboxylic acids in the copolymers increased, the residue, found at 600 °C, increased. The copolymers of styrene and the sodium or potassium salt of vinylbenzoic acid formed more residue than the acid form of the copolymers. The copolymers behaved independently and showed two transitions: one for the polystyrene depolymerization and one for the decarboxylation of the salt. Qualitatively, the decomposition pathways of the salts in the polymer matrix appear to be similar to that of the simple benzoate salts but slightly more residue was formed in the copolymers. However, the mass spectral data from the TG-MS of the copolymers and their salts needs to be investigated in more detail to determine if there is any difference in the product distributions, since in cation exchanged low-rank coal, the aliphatic/aromatic product ratio was altered by cation exchange.⁸ Although the sodium and potassium benzoates form more residue than the calcium benzoate, it is predicted that the calcium carboxylates would produce more cross-links (as ketones) than the sodium or potassium salts, which disproportionation. This trend is observed in pyrolysis and liquefaction of cation-exchanged low-rank coals with lower liquid yields (i.e., more cross-linking) reported for $\text{Na}^+ < \text{K}^+ < \text{Ca}^{2+}$ salts.^{1,4} We are currently preparing calcium salts of additional copolymers to determine if ketone formation is responsible for cross-linking.

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